

Highly-confined spin-polarized two-dimensional electron gas in $\text{SrTiO}_3/\text{SrRuO}_3$ superlattices

Marcos Verissimo-Alves,¹ Pablo García-Fernández,¹ Daniel I. Bilc,² Philippe Ghosez,² and Javier Junquera¹

¹*Departamento de Ciencias de la Tierra y Física de la Materia Condensada,
Universidad de Cantabria, Cantabria Campus Internacional,
Avenida de los Castros s/n, 39005 Santander, Spain*

²*Physique Théorique des Matériaux, Université de Liège,
Allée du 6 de Août 17 (B5), B-4000 Sart Tilman, Belgium*

(Dated: January 17, 2012)

We report first principles characterization of the structural and electronic properties of $(\text{SrTiO}_3)_5/(\text{SrRuO}_3)_1$ superlattices. We show that the system exhibits a spin-polarized two-dimensional electron gas, extremely confined to the $4d$ orbitals of Ru in the SrRuO_3 layer. Every interface in the superlattice behaves as a minority-spin half-metal ferromagnet, with a magnetic moment of $\mu = 2.0 \mu_B/\text{SrRuO}_3$ unit. The shape of the electronic density of states, half metallicity and magnetism are explained in terms of a simplified tight-binding model, considering only the t_{2g} orbitals plus (i) the bi-dimensionality of the system, and (ii) strong electron correlations.

PACS numbers: 74.70.Pq, 73.20.At, 75.70.-i, 75.10.-b

The family of ABO_3 perovskite compounds is really prominent among all the complex oxides. The delicate interaction between their electronic, spin, lattice and orbital ordering degrees of freedom, whose respective energy couplings are all of the same order of magnitude [1], gives rise to a wide variety of ground states and phenomena [2]. These compounds typically exhibit exceptional functional properties that, moreover, can be finely tuned by playing with temperature and/or electrical (screening) [3], mechanical (strain) [4], and chemical (doping) [5] boundary conditions.

At the bulk level, ABO_3 compounds cover the whole spectrum of conducting properties, ranging from good insulators and semiconductors to metals and even superconductors [2]. Moreover, it has recently been shown that their conducting behaviour can also drastically change at surfaces [6] and interfaces [7]. The possibility to create highly-confined two-dimensional electron gases (2DEGs) at oxide interfaces has also been demonstrated and generated a huge excitement.

The most widely studied system is certainly the 2DEG formed at the LaO/TiO_2 polar interface between LaAlO_3 (LAO) and SrTiO_3 (STO) [8], two good band insulators at the bulk level. Although the mechanism at the origin of the transfer of charges remains partly controversial, the 2DEG is formed by the accumulation of electrons in the Ti $3d$ states of STO over a thickness of a few nanometers near the interface, and exhibits interesting exotic properties. In a different context, when looking for oxides with enhanced thermoelectric properties, Ohta *et al.* [9] highlighted the possibility to create a highly-confined 2DEG in $[(\text{STO})_m/(\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3)_n]_p$ superlattices. Since Nb-doped STO is a well-known conducting electrode material [10], such a superlattice can be viewed as the limiting case of ultrathin metal oxide layers embedded in an insulating STO matrix. The 2DEG arises

from the doping produced by the Nb atoms so, alternatively, the system can also be interpreted as a *partial* doping of a STO matrix at the B site. Very recently, the formation of a 2DEG has been achieved through a related route: the doping of the A site of the STO matrix. The Sr atoms of a single SrO layer of STO are partially [11] or completely [12] replaced by a rare-earth element, R , which provides additional electrons. In this case, the conduction electrons provided by the substitutional layer are transferred to the STO matrix but stay near the RO layer due to Coulomb attractions, and possibly also to the large dielectric constant of STO [13].

In this Letter, we predict from first principles calculations the appearance of a highly-confined 2DEG in $(\text{STO})_5/(\text{SrRuO}_3)_1$ superlattices (STO/SRO). This system is to some extent related to those previously considered. SRO is a well-known conductive material so that STO/SRO present similarities with $(\text{STO})_m/(\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3)_n$ superlattices [9]. Also, STO/SRO can be seen as a STO matrix in which a TiO_2 layer is periodically replaced by a single RuO_2 layer, appearing as a variant of the work of Jang *et al.* [12]. However, contrary to all recent examples of 2DEGs in perovskites previously discussed, that confine the conducting electrons in Ti $3d$ orbitals of STO, the conducting electrons in STO/SRO are localized *exclusively* in Ru $4d$ orbitals. We will show that this gives rise to new and unexpected features. Contrary to current though regarding SRO *thin films* [14–16], and *finite period* superlattice [17], our infinite period superlattices exhibits an extremely confined half-metallic ferromagnetic (FM) 2DEG, very promising for spintronic devices [18].

For this study, we perform first principles simulations of STO/SRO superlattices using two complementary approaches. Unless otherwise stated, all the calculations presented here have been performed within the local spin

density approximation (LSDA) to the density functional theory using the SIESTA code [19]. An extra Hubbard-U term is included to account for the strong electron correlations, with a U_{eff} of 4.0 eV applied only to the d orbitals of Ru. The robustness of the results presented below have been doubled checked using the CRYSTAL09 code [20] within the B1-WC hybrid scheme [21]. Hybrid functionals are well known to provide improved description of magnetic and highly-correlated oxides, and B1-WC appeared recently as a successful approach to describe 2DEG at the LAO/STO interface [22]. The excellent agreement between the results obtained independently within both approaches strongly supports our predictions. The procedure to fit the U_{eff} and other technicalities can be found in the Discussion 1 and 2 of the Supplemental materials [23]. Both spin-orderings in the SRO layers, FM and antiferromagnetic (AFM), where the up and down spins of the RuO_2 layer are ordered in a checkerboard arrangement, are simulated.

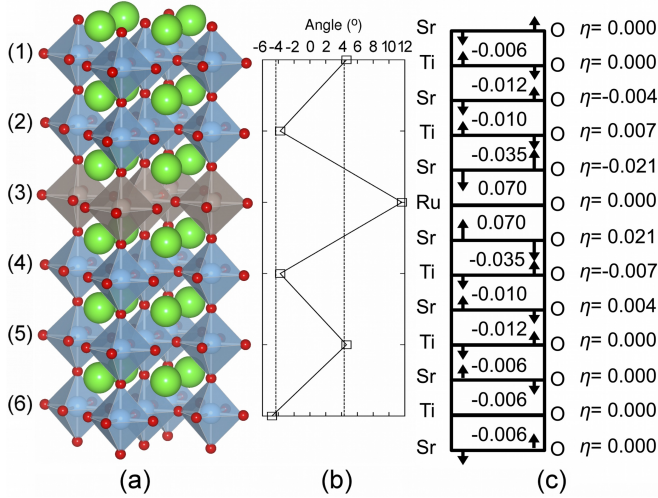


FIG. 1. (color online) Schematic representation of the relaxed structure of STO/SRO superlattices with LDA+U. (a) Unit cell periodically repeated in space. O atoms are shown in red, Sr in blue, Ti in grey and Ru in grey, with O octahedra colored accordingly. (b) Rotation angle of the oxygen octahedra, θ , around the [001] direction (z axis). Squares represent θ for the corresponding octahedra at the same height as in panel (a). Dotted lines are the theoretical value of θ for bulk STO. (c) Layer-by-layer rumpling, $\eta_i = [z(M_i) - z(O_i)]/2$, where $z(M_i)$ is the position of the cation, and $z(O_i)$ is the position of O, in a given layer i . Atoms in layer i move in the direction indicated by the arrows. Black lines represent the mean position of each atomic layer. Numbers inside the structure are the change in the interplanar distance between consecutive planes with respect to the ideal unrelaxed structure (half of the bulk value of STO, $a = 3.874$ Å). Similar results are obtained within the B1-WC functional (see Discussion 3 of the Supplemental material [23]). Units in Å.

In the most stable phase, that turns out to have FM order, our simulations predict a $P4/mbm$ space group.

Oxygen octahedra rotate changing the phase from layer to layer, as shown in Fig. 1(b). This pattern of rotation shares some similarities with the $a^0a^0c^-$ Glazer rotation of the STO matrix, but now the module of the rotation angles around the z -axis are not the same from one octahedra to the adjacent one. The angle of rotation of the RuO_6 octahedra, $\theta_{\text{SRO}} = 11.6^\circ$, is roughly the same as in bulk tetragonal SRO under the same strain condition in the basal plane ($\theta_{\text{SRO}}^{\text{bulk}} = 11.4^\circ$). The rotations of the TiO_6 octahedra rapidly converge to the bulk LDA value of STO ($\theta_{\text{STO}}^{\text{bulk}} = 4.3^\circ$), indicating that the rotations are functions of the local chemical environment [24]. Taking into account that bulk SRO crystallizes within the GdFeO_3 structure ($Pnma$ space group), with $a^-b^+a^-$ Glazer rotation, we have explored the possibility of the existence of out-of-plane tiltings in SRO. However, under the epitaxial configuration considered here, we have checked that they disappear. This supports that the single unit cell of SRO in our superlattices are stabilized in a pseudocubic perovskite structure [25]. As shown in Fig. 1(c), both the rumplings, and the changes in interplanar spacing with respect to the ideal (non-relaxed) structure, are very small.

Figure 2 shows the projected density of states (PDOS) on the atoms at the different SrBO_3 unit cells (where B is Ti or Ru), within the LDA+U [panel (a)], and B1-WC hybrid functional [panel (b)]. The physical conclusions that can be drawn are robust, independently of the theoretical framework used. In particular: (i) remarkably the system presents a 2DEG, strictly confined in the SRO layer. The electronegativity of Ru (2.20), larger than the one for Ti (1.54), is the main candidate to be the driving force for the electron localization. This localization resembles that recently found on the d orbitals of V in $\text{SrVO}_3/\text{Nb:SrTiO}_3$ quantum wells [26]. (ii) The electronic states around the Fermi level are fully spin-polarized, with only the minority-spin electrons involved in the charge transport [18]. (iii) The 2DEG exhibits ferromagnetism, with a magnetic moment of $\mu = 2.0 \mu_B/\text{SRO}$ formula unit. Integrating the spin-polarized charge density on spheres surrounding the atoms (in SIESTA) or analyzing the Mulliken spin population within B1-WC (in CRYSTAL), we see that the magnetic moment is mostly due to the Ru atoms, $\mu_{\text{Ru}} = 1.4 \mu_B$, within the range of measured magnetic moments in single crystals [27], and polycrystalline samples [28]. The same value of μ_{Ru} is obtained in the AFM configuration. The remaining magnetic moment in the FM configuration comes from the oxygen atoms. These results are robust with respect to pseudopotentials, basis set, functional, and inclusion of spin-orbit coupling (Discussion 4 of the Supplemental material [23]). Interestingly, the electronic structure at the interface inherits some of the particularities theoretically predicted in *bulk* SRO when the electronic correlations are properly included [as in LDA+U [29], pseudo self-interaction correction [30], or

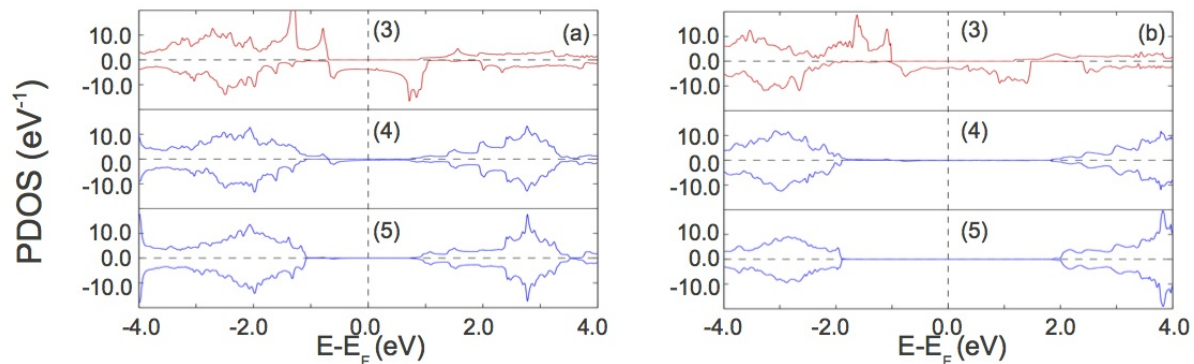


FIG. 2. (color online) Layer-by-layer PDOS on the atoms at the SrBO_3 layers ($B = \text{Ti}$ or Ru), within (a) the LSDA+U, and (b) the B1-WC hybrid functional, for the corresponding relaxed STO/SRO superlattice. Each panel represents the PDOS of a unit cell, numbered as in Fig. 1(a). Corresponding layers in the upper-half of the structure are equivalent by symmetry. Majority/minority spin are represented in the upper/lower halves of each panel, respectively.

B1-WC hybrid functional (Discussion 5 in the Supplemental materials [23]). Between these properties, we might cite the half-metallicity [29] or the saturation of the magnetic moment [30]. Experimental observation of the half-metallicity remains a challenge, mostly due to the large magnetic fields required to overcome the high magnetic anisotropy barriers and fully magnetize the samples.

Regarding the band shape, we observe in Fig. 3 that the bands with $\text{Ru-}d_{xy}$ character are significantly different from the degenerate $\text{Ru-}d_{xz,yz}$ bands. While the PDOS of $\text{Ru-}d_{xy}$ resembles that usually found in bulk t_{2g} bands [31], the double peaked shape [peaks marked with arrows in Fig. 3(b)] for $\text{Ru-}d_{xz,yz}$ is similar to that of a 1D metal. It is also significant that the relative position of these bands for the majority and minority spins is different, an effect attributable to the strong electronic correlations in the system, enhanced with respect to bulk due to the two-dimensionality of the system (see below). Indeed, to study the effect of the Hubbard-U in our calculations we carried out a plain LSDA simulation (without U corrections) and plotted the PDOS (Discussion 2 in the Supplemental materials [23]). The *shape* of the $\text{Ru-}d_{xy}$ and $\text{Ru-}d_{xz,yz}$ is the same as when the Hubbard-U term is considered. However, the position of the bands is shifted to almost the same energy range for both spin channels, destroying the half-metallicity.

If the half-metallicity can be attributed to the electronic correlation, the shape of the bands can only be explained through the 2D character of the electron gas. To check this point, we have made use of a tight-binding model, where only the t_{2g} states are retained in the basis set. Qualitatively, the shape of the t_{2g} bands is found to be the same for all perovskites including transition metal ions in the B-position. Assuming cubic symmetry, the PDOS associated to these bands for a full three-dimensional solid is shown in Fig. 4(a). Using this model

we then simulate the changes in the PDOS when the system is bidimensional, extended periodically through the xy plane. In Fig. 4(b) we can see that, while d_{xy} -band remains unaltered, the $d_{xz,yz}$ ones now present two-peaks in good agreement with the ones in the full first principles calculations [arrows in Fig. 3(b)]. In particular, the PDOS of bidimensional $d_{xz,yz}$ levels closely resembles that of textbook one-dimensional electron gas [31] due to the negligible interactions of $d_{xz,yz}$ wavefunctions in the xy plane with other than first neighbors. However, we can observe that the LDA+U bands are shifted with respect to the ones obtained in our tight-binding model. These shifts are due to (i) the difference in bonding of the orbitals with in-plane and out-of-plane neighbors and (ii) the Hubbard-U correction. To take into account the first effect we note that the d_{xy} wavefunctions only interact strongly with in-plane neighbors which are all functions centered around Ru^{4+} ions. In contrast, $d_{xz,yz}$ wavefunctions interact in-plane with centers around Ru^{4+} ions while out-of-plane they interact with functions centered on Ti^{4+} ions mediated by O atoms [see Fig. 4(e)]. Since Ru^{4+} ions are more electronegative than Ti^{4+} ones, the apical oxygens are polarized towards the Ru^{4+} . This translates into an increase of covalency and, therefore, a decrease in the energy of the bonding states and an increase of the antibonding levels, denoted as ΔE_{cov} in Fig. 4(c). Finally, we include the effect of the U_{eff} value to take into account magnetism. LDA+U theory predicts that orbital energies are shifted by $U_{\text{eff}}(1/2 - \lambda)$ where λ is the occupation of the orbital. Using this formula, and assuming that the majority spin t_{2g} levels are full, while the minority spin d_{xz} , d_{yz} and d_{xy} contain respectively 0.5, 0.5 and 0.0 electrons, we find the shifts depicted in Fig. 4(d). Qualitatively, we find the bands to be in good agreement with those obtained in the full first-principles calculations [see Fig. 3(b)].

In summary, our first principles simulations pre-

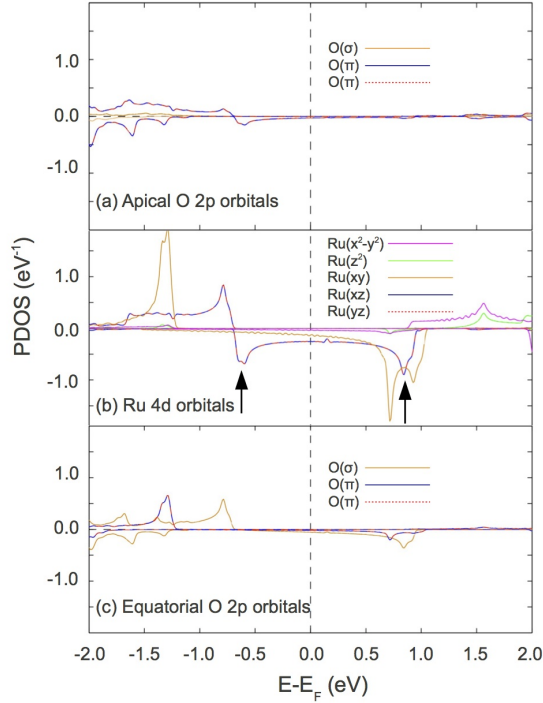


FIG. 3. (Color online) PDOS on the atoms at the central SRO layer, projected on the orbitals of (a) an apical O atom, (b) the Ru atom, and (c) an equatorial O atom. In the DOS projections corresponding to Oxygen, the $2p$ orbital directed towards the transition metal ions is denoted by $O(\sigma)$, while the two quasi-degenerate orbitals perpendicular to this bond direction are $O(\pi)$. The arrows in panel (b) mark the position of the peaks for the $Ru-d_{xz,yz}$ orbitals (see text).

dict the appearance of a two-dimensional, half-metallic, ferromagnetically ordered electron gas at the insulator/ultrathin-metal-film interfaces in $(STO)_5/(SRO)_1$ superlattices. The 2DEG is extremely confined at Ru $4d$ orbitals. At odds with previous realizations of 2DEG, where the main mechanism behind localization is of electrostatic nature [13, 22], we propose the larger electronegativity of Ru to be the main cause for the extreme confinement. The half-metallic properties and the concomitant FM is an intrinsic property due to enhanced electron correlation, and not to extrinsic properties (O vacancies) as postulated in LAO/STO 2DEG [32]. Our results encourage experimental verification, to check the usefulness of these superlattices in magnetoresistance or spintronic devices.

Financial support from grants FIS2009-12721-C04-02, and CP-FP 228989-2 OxIDES. Calculations were performed on the computers at the ATC group and on the Altamira Supercomputer of the RES.

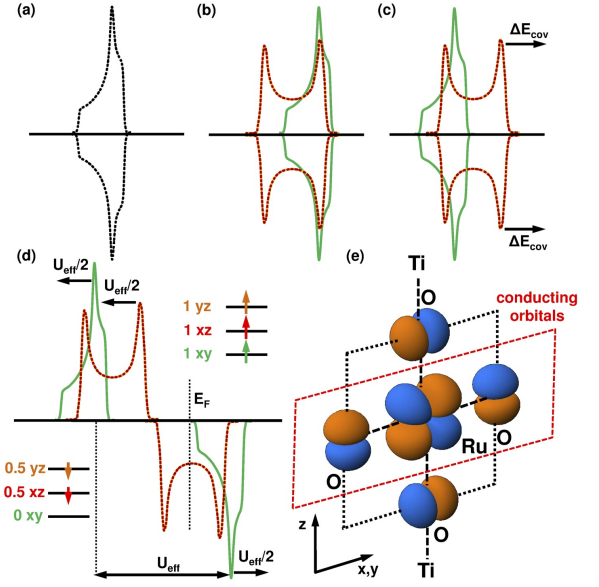


FIG. 4. (Color online) Result of the tight-binding model used to interpret the DOS of t_{2g} d orbitals. Our model shows the transformation from (a) the three-dimensional bulk, to (b) a two-dimensional structure. Refinements of the model to include, first, covalent bonding effects in-plane and out-of-plane (c), and second, shifts of the bands due to strong electronic correlation via a Hubbard- U term (d), are required to reproduce the first principles band structure. Black lines in (a) represent the $d_{xy,xz,yz}$ manifold, degenerated in energy. Once the symmetry is broken, the d_{xy} state is represented by a green line, and the degenerated $d_{xz,yz}$ orbitals by red lines. (e) illustrates the orbitals used in the tight-binding model and differences of in-plane and out-of-plane bonding for d_{xz} orbitals (identical sketch can be done for the d_{yz} orbitals).

-
- [1] J. M. Rondinelli and N. A. Spaldin, *Adv. Mater.*, **XX**, 1 (2011).
 - [2] P. Zubko et al., *Annu. Rev. Condens. Matter Phys.*, **2**, 141 (2011).
 - [3] M. Stengel, N. A. Spaldin, and D. Vanderbilt, *Nat. Phys.*, **5**, 304 (2009).
 - [4] D. G. Schlom et al., *Annu. Rev. Mater. Res.*, **37**, 589 (2007).
 - [5] R. V. Wang et al., *Phys. Rev. Lett.*, **102**, 047601 (2009).
 - [6] A. F. Santander-Syro et al., *Nature (London)*, **469**, 189 (2011).
 - [7] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, *Nature*, **419**, 378 (2002).
 - [8] A. Ohtomo and H. Y. Hwang, *Nature (London)*, **427**, 423 (2004).
 - [9] H. Ohta et al., *Nat. Mater.*, **6**, 129 (2007).
 - [10] T. Tybell, C. H. Ahn, and J.-M. Triscone, *Appl. Phys. Lett.*, **75**, 856 (1999).
 - [11] P. V. Ong, J. Lee, and W. E. Pickett, *Phys. Rev. B*, **83**, 193106 (2011).

- [12] H. W. Jang et al., *Science*, **331**, 886 (2011).
- [13] M. Stengel, *Phys. Rev. Lett.*, **106**, 136803 (2011).
- [14] P. Mahadevan, F. Aryasetiawan, A. Janotti, and T. Sasaki, *Phys. Rev. B*, **80**, 035106 (2009).
- [15] Y. J. Chang et al., *Phys. Rev. Lett.*, **103**, 057201 (2009).
- [16] J. Xia et al., *Phys. Rev. B*, **79**, 140407(R) (2009).
- [17] M. Izumi, K. Nakazawa, and Y. Bando, *J. Phys. Soc. Jpn.*, **67**, 651 (1998).
- [18] T. K. Mandal and M. Greenblatt, “Functional oxides,” (John Wiley & Sons, Ltd., West Sussex, United Kingdom, 2010) pp. 257–293.
- [19] J. M. Soler et al., *J. Phys.: Condens. Matter*, **14**, 2745 (2002).
- [20] See the CRYSTAL web page: <http://www.crystal.unito.it>.
- [21] D. I. Bilc et al., *Phys. Rev. B*, **77**, 165107 (2008).
- [22] P. Delugas et al., *Phys. Rev. Lett.*, **106**, 166807 (2011).
- [23] See Supplemental Material for methods and supplemental data.
- [24] X. Wu, K. M. Rabe, and D. Vanderbilt, *Phys. Rev. B*, **83**, 020104(R) (2011).
- [25] C. B. Eom et al., *Science*, **258**, 1766 (1992).
- [26] K. Yoshimatsu et al., *Science*, **333**, 319 (2011).
- [27] G. Cao et al., *Phys. Rev. B*, **56**, 321 (1997).
- [28] C.-Q. Jin et al., *PNAS*, **105**, 7115 (2008).
- [29] H.-T. Jeng, S.-H. Lin, and C.-S. Hsue, *Phys. Rev. Lett.*, **97**, 067002 (2006).
- [30] J. M. Rondinelli, N. M. Caffrey, S. Sanvito, and N. A. Spaldin, *Phys. Rev. B*, **78**, 155107 (2008).
- [31] T. Wolfram and S. Ellialtıoğlu, *Electronic and optical properties of d-band perovskites* (Cambridge University Press, Cambridge, 2006).
- [32] A. Brinkman et al., *Nat. Mater.*, **6**, 493 (2007).